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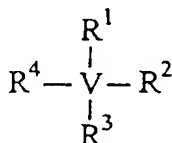
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(54) Olefin polymerization process and catalyst system therefor

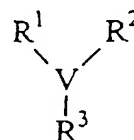
(57) An olefin monomer polymerization catalyst system is described. The catalyst system comprises:

(i) a vanadium catalyst having the formula:



wherein:

R^1 , R^2 , R^3 and R^4 are the same or different and each is selected from a halogen and $-(NR^5R^6)$, R^5 and R^6 are the same or different and each is selected from the group comprising an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and a silicon-containing hydrocarbyl group, and R^1 and R^2 may be combined to form a cyclic moiety, with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is $-(NR^5R^6)$, or the formula:



wherein:

R^1 , R^2 and R^3 are as defined above, with the proviso that at least one of R^1 , R^2 and R^3 is $-(NR^5R^6)$;

(ii) an organoaluminum cocatalyst; and

(iii) a catalyst activator having the formula:



wherein M is a metal selected from Group 2 and Group 12 of the Periodic Table, R^7 is a C_1 - C_{12} alkyl group and n is a number equal to the valence of M. At least one of the vanadium catalyst and organoaluminum cocatalyst contains a halogen moiety. A process for polymerizing an olefin using the catalyst system is also described.

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Description

TECHNICAL FIELD

5 [0001] The present invention relates to an olefin polymerization catalyst and to a process for olefin polymerization.

BACKGROUND ART

10 [0002] The polymerization of olefins is well known in the art. It is known to produce both crystalline and amorphous polyolefins via the so-called Ziegler-Natta polymerization process.

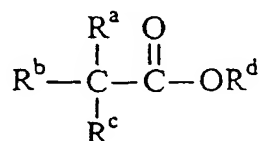
[0003] Generally, the polymerization reaction is catalysed through the use of a transition metal catalyst compound and a cocatalyst compound. More specifically, it is conventional to produce EPDM (ethylene-propylene-diene-methylene) terpolymers and EPM (ethylene-propylene-methylene) copolymers in solution or slurry processes using Ziegler-Natta catalysts such as VOCl_3 , $\text{V}(\text{acac})_3$ (acac/acetyl acetone) and VCl_4 , in combination with an aluminum-based cocatalyst such as diethyl aluminochloride (DEAC) and/or ethyl aluminum sesquichloride (EASC) and/or ethyl aluminum dichloride (EADC).

20 [0004] A problem with these vanadium catalyst systems is "catalyst decay" as a function of polymerization time and temperature. In other words, these vanadium catalysts do not show constant activity during polymerization of the olefinic monomers. Simply increasing the polymerization temperature to obviate this problem results in a decrease in catalyst activity.

[0005] Over the years, the mechanistic aspects of EPDM polymerization with various vanadium compounds (+3 and +5 valent) have been studied. During polymerization, the vanadium compounds are readily reduced to V^{+2} upon addition of the aluminum alkyl halide cocatalyst. As discussed above, simply increasing the polymerization temperature also results in reduction of the vanadium oxidation state to +2. Unfortunately, the +2 oxidation state of the vanadium is not an active oxidation state for olefinic polymerization (e.g., EPM or EPDM polymerization). Rather, +3 is oxidation state of vanadium which is active in this polymerization. The inactivated V^{+2} can be activated or reactivated by the addition of chlorinated hydrocarbons such as those having the general formula:

wherein:

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40 R^a and R^b may be the same or different and are a halogen;
 R^c is selected from the group comprising halogen, an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and an ester group; and
 R^d is selected from the group comprising an alkyl group, an aryl group and an alkenyl group. Non-limiting examples of useful such chlorinated hydrocarbons include ethyl-trichloroacetate (ETA) and dichlorophenyl ethyl acetate (DCPEE).

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[0006] The prior art has attempted to overcome these problems using a variety of approaches.

[0007] United States patent 3,711,455 [Cucinella et al. (Cucinella)], the contents of which are hereby incorporated by reference, teaches a process for the preparation of copolymers of a monoolefin and a diolefin and the products obtained thereby. Generally, the point of novelty taught by Cucinella relates to the use of a catalyst system comprising:

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(i) a vanadium compound of the type $\text{V}(\text{NR}_2)_4$ or $\text{V}(\text{NR}_2)_2\text{X}_2$ wherein R may be an alkyl, aryl or cycloalkyl radical and X a halogen such as Cl, Br or I; and

(ii) an aluminum compound of the type $\text{AlR}_x\text{X}_{3-x}$ wherein R may be an alkyl, aryl or cycloalkyl radical or hydrogen and X a halogen such as Cl, Br or I, wherein $1 \leq x \leq 2$

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- see column 1, lines 48-57. Cucinella teaches that the advantage accruing from the use of this catalyst is production of a true copolymer of monoolefin and diolefin (i.e., as compared to contemporaneous production of individual homopol-

ymers of the starting monomers) in good yield which is capable of being crosslinked when subjected to curing.

[0008] Published European patent application 0,532,098 [Renkema et al. (Renkema #1)], the contents of which are hereby incorporated by reference, teaches a catalyst and a process for the preparation of an olefin polymer. Generally, the point of novelty taught by Renkema #1 relates to the use of a catalyst comprising a transition metal atom onto which is bound an imidoaryl ligand - see page 2, lines 21-24.

[0009] International publication number WO94/14854 [Renkema et al. (Renkema #2)], the contents of which are hereby incorporated by reference, teaches a catalyst and a process for Ziegler polymerization. Generally, the point of novelty taught by Renkema #2, which appears to build on the teachings of Renkema #1, relates to the use of a catalyst system comprising a transition metal-imidoaryl complex containing at least one amido group bound to the transition metal, the aryl group in the complex being an *o,o*-disubstituted phenyl group - see page 1, lines 31-36. Renkema #2 further teaches that the combination of the amido group and the imido, *o,o*-disubstituted phenyl group both bound to the transition metal results in a catalyst having both high activity and good stability-see page 1, line 37 to page 2, line 16.

[0010] Notwithstanding these prior art approaches there is a continuing need in the art for a catalyst system which can be used in olefin polymerization (e.g., EPM and EPDM) and possess improved catalyst activity/efficiency.

DISCLOSURE OF THE INVENTION

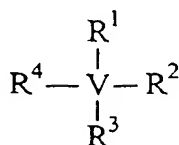
[0011] It is an object of the present invention to provide a novel process for production of an olefin polymer which obviates or mitigates at least one of the above-identified disadvantages of the prior art.

[0012] It is another object of the present invention to provide a novel olefin monomer polymerization catalyst system which obviates or mitigates at least one of the above-identified disadvantages of the prior art.

[0013] It is another object of the present invention to provide a novel olefin polymerization catalyst system kit which obviates or mitigates at least one of the above-identified disadvantages of the prior art.

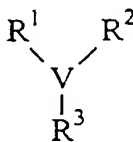
[0014] Accordingly, in one of its aspects, the present invention provides a process for production of an olefin polymer comprising the step of polymerizing an olefin monomer in the presence of a catalyst system comprising:

(i) a vanadium catalyst having the formula:



wherein:

R^1 , R^2 , R^3 and R^4 are the same or different and each is selected from a halogen and $-(NR^5R^6)$, R^5 and R^6 are the same or different and each is selected from the group comprising an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and a silicon-containing hydrocarbyl group, and R^1 and R^2 may be combined to form a cyclic moiety, with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is $-(NR^5R^6)$, or the formula:



wherein:

R^1 , R^2 and R^3 are as defined above, with the proviso that at least one of R^1 , R^2 and R^3 is $-(NR^5R^6)$;

(ii) an organoaluminum cocatalyst; and

(iii) a catalyst activator having the formula:

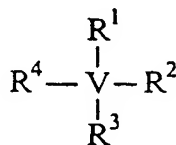


wherein M is a metal selected from Group 2 and Group 12 (New notation of the Periodic Table of Elements as noted in the CRC Handbook of Chemistry and Physics (70th Edition)) of the Periodic Table, R^7 is a C_1 - C_{12} alkyl group and n is a number equal to the valence of M;

wherein at least one of the vanadium catalyst and organoaluminum cocatalyst contains a halogen moiety.

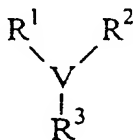
[0015] In another of its aspects, the present invention provides an olefin monomer polymerization catalyst system, the system comprising:

(i) a vanadium catalyst having the formula:



wherein:

R^1 , R^2 , R^3 and R^4 are the same or different and each is selected from a halogen and $-(NR^5R^6)$, R^5 and R^6 are the same or different and each is selected from the group comprising an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and a silicon-containing hydrocarbonyl group, and R^1 and R^2 may be combined to form a cyclic moiety, with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is $-(NR^5R^6)$, or the formula:



wherein:

R^1 , R^2 and R^3 are as defined above, with the proviso that at least one of R^1 , R^2 and R^3 is $-(NR^5R^6)$;

(ii) an organoaluminum cocatalyst; and

(iii) a catalyst activator having the formula:

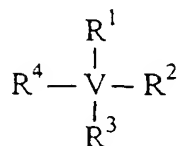


wherein M is a metal selected from Group 2 and Group 12 of the Periodic Table, R^7 is a C_1 - C_{12} alkyl group and n is a number equal to the valence of M;

wherein at least one of the vanadium catalyst and organoaluminum cocatalyst contains a halogen moiety.

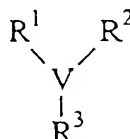
[0016] In yet another of its aspects, the present invention provides an olefin polymerization catalyst system kit comprising, as individual components:

(i) a vanadium catalyst having the formula:



wherein:

R^1 , R^2 , R^3 and R^4 are the same or different and each is selected from a halogen and $-(NR^5R^6)$, R^5 and R^6 are the same or different and each is selected from the group comprising an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and a silicon-containing hydrocarbyl group, and R^1 and R^2 may be combined to form a cyclic moiety, with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is $-(NR^5R^6)$, or the formula:



wherein:

R^1 , R^2 and R^3 are as defined above, with the proviso that at least one of R^1 , R^2 and R^3 is $-(NR^5R^6)$;

- (ii) an organoaluminum cocatalyst; and
- (iii) a catalyst activator having the formula:



wherein M is a metal selected from Group 2 and Group 12 of the Periodic Table, R^7 is a C_1 - C_{12} alkyl group and n is a number equal to the valence of M;

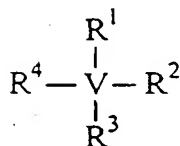
wherein at least one of the vanadium catalyst and organoaluminum cocatalyst contains a halogen moiety.

[0017] Thus, it has been discovered that the combination of a specific class of vanadium catalysts with a specific class of catalyst activator compounds surprisingly and unexpectedly results in: (i) a significant improvement in catalyst activity, and (ii) desirable molecular weight control of the resulting polymer. As will be developed herein below, this discovery is surprising and unexpected because the specific class of catalyst activator compounds, when used with other classes of vanadium catalysts, in fact reduces the activity of such other vanadium catalysts.

BEST MODE FOR CARRYING OUT THE INVENTION

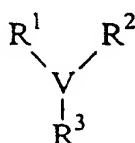
[0018] Thus, the present catalyst system comprises: a vanadium catalyst, an organoaluminum cocatalyst and a catalyst activator.

[0019] The vanadium catalyst has the formula:



wherein:

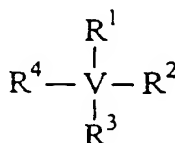
R^1 , R^2 , R^3 and R^4 are the same or different and each is selected from a halogen and $-(NR^5R^6)$, R^5 and R^6 are the same or different and each is selected from the group comprising an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and a silicon-containing hydrocarbyl group, and R^1 and R^2 may be combined to form a cyclic moiety, with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is $-(NR^5R^6)$, or the formula:



wherein:

R^1 , R^2 and R^3 are as defined above, with the proviso that at least one of R^1 , R^2 and R^3 is $-(NR^5R^6)$. Such compounds are known in the art and the preparation thereof will be apparent to those of skill in the art.

[0020] Preferably, the vanadium catalyst has the formula:



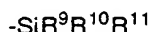
wherein:

R^1 , R^2 , R^3 and R^4 are as described hereinabove.

[0021] In one preferred embodiment, R^1 , R^2 , R^3 and R^4 are the same or different and each $-(NR^5R^6)$ (i.e., in this preferred embodiment, the organoaluminum cocatalyst contains a halogen moiety). In another preferred embodiment, R^1 , R^2 and R^3 are the same or different and each is $-(NR^5R^6)$, and R^4 a halogen. In yet another preferred embodiment, R^1 and R^2 are the same or different and each is $-(NR^5R^6)$, and R^3 and R^4 are the same or different and each is a halogen. In yet another preferred embodiment, R^1 is $-(NR^5R^6)$, and R^2 , R^3 and R^4 are the same or different and each is a halogen.

[0022] In one preferred embodiment, at least one (more preferably each) of R^5 and R^6 is selected from the group comprising a C_2 - C_8 alkyl group, a C_5 - C_{20} aryl group and a C_3 - C_{20} cycloalkyl group. More preferably, at least one (even more preferably both) of R^5 and R^6 is selected from the group comprising an ethyl group, a propyl group, an *i*-propyl group, a butyl group and a cyclohexyl group. It is preferred, for a given vanadium catalyst, that R^5 and R^6 are the same.

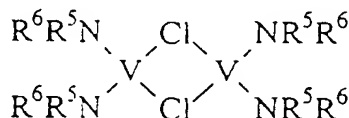
[0023] In another preferred embodiment, at least one (more preferably each) of R^5 and R^6 is a silicon-containing hydrocarbyl group having the following formula:



wherein R^9 , R^{10} and R^{11} are the same or different and each is selected from the group comprising a C_2 - C_8 alkyl group, a C_5 - C_{20} aryl group and a C_3 - C_{20} cycloalkyl group.

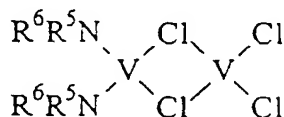
[0024] Of course, the halogen moiety on the vanadium catalyst, if present, may be selected from the group comprising fluoride, bromide, chloride, iodide and astatine. The preferred halogen moiety is chloride. If two or more halogen moieties are present on the vanadium catalyst, it is preferred that they be the same.

[0025] As indicated above, R^1 and R^2 may be combined to form a cyclic moiety. Thus, it is intended to include within the scope of the vanadium catalyst useful herein bis-vanadium derivatives comprising one, preferably two, bridging groups between the two vanadium atoms. In a first embodiment, R^1 and R^2 may be combined to form an organic or organometallic cyclic moiety (i.e., the combination of at least R^1 , R^2 and V form a ring). In a second embodiment, R^1 and R^2 may be combined to form an inorganic cyclic moiety. A non-limiting example of the second embodiment is a compound having the formula:



wherein:

R^5 and R^6 are as defined hereinabove. This compound may be produced by reaction of $VCl_3(THF)_3$ with a two-fold molar excess of a compound of the formula R^5R^6NLi with heating. Another non-limiting example of the second embodiment is a compound having the formula:

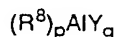


wherein:

R^5 and R^6 are as defined hereinabove. This compound may be produced by reaction of $VCl_3(THF)_3$ with an equimolar amount of a compound of the formula R^5R^6NLi .

[0026] Thus, when the vanadium catalyst is tetravalent (i.e., each of R^1 , R^2 , R^3 and R^4 are present) and contains no chlorine bridges as described above, the vanadium is in a +4 oxidation state. When the vanadium catalyst is: (i) tetravalent and contains chlorine bridges as described above, or (ii) trivalent (i.e., only R^1 , R^2 and R^3 are present), the vanadium is in a +3 oxidation state. A vanadium catalyst as described above and having these oxidation states is useful within the scope of the present invention. As will be appreciated by those of skill in the art, from a practical perspective, it is very difficult to obtain the vanadium catalyst in a pure (i.e., 100%) form. Thus, while the preferred form of vanadium catalyst for use herein is in the +4 oxidation state, the catalyst used may typically contain minor amounts (i.e., up to 20 percent by weight, more likely up to 10 percent by weight) of vanadium catalyst in the +3 oxidation state. Such catalyst mixtures are intended to be included within the spirit and scope of the present invention.

[0027] The second component of the present catalyst system is an organoaluminum cocatalyst. The use of organoaluminum cocatalysts in Ziegler-Natta polymerization processes is conventional and the choice of organoaluminum cocatalyst to be used in the present catalyst system is within the purview of a person skilled in the art. Preferably, the organoaluminum cocatalyst comprises at least one compound having the formula:



wherein R^8 is selected from the group comprising a C_2 - C_{20} alkyl group, a C_2 - C_{10} alkoxy group and a C_3 - C_{20} cycloalkyl group, Y is selected from the group comprising R^8 and a halogen and $p+q$ is 3 (as will be developed below, p and q need not necessarily be integers). Preferably, the organoaluminum cocatalyst comprises a mixture of at least two of said compounds.

[0028] Preferably, p is a number in the range of from 1 to 2, and q is a number in the range of from 0 to 2, again with the proviso that p+q is 3. In a more preferred embodiment, p is 2 and q is 1. In another more preferred embodiment, p and q are 1.5. In yet another more preferred embodiment, q is 1 and p is 2.

[0029] Preferably, R⁸ is ethyl.

5 [0030] Preferably Y is a halogen. Of course, the halogen Y in the preferred formula for the organoaluminum cocatalyst may be selected from the group comprising fluoride, bromide, chloride, iodide and astatine. The preferred halogen moiety is chloride. If two or more halogen moieties are present on the organoaluminum cocatalyst, it is preferred that they be the same.

10 [0031] Non-limiting examples organoaluminum cocatalysts useful in the present invention may be selected from the group comprising trimethylaluminum, triethylaluminum, diethyl aluminum hydride, triisobutyl aluminum, tridecyl aluminum, tridodecyl aluminum, diethyl aluminum methoxide, diethyl aluminum ethoxide, diethyl aluminum phenoxide, diethyl aluminum chloride, ethyl aluminum dichloride, ethyl aluminum sesquichloride, diisobutylaluminum chloride, dioctylaluminum chloride, octylaluminum sesquichloride, methyl diethoxy aluminum, methyl aluminoxane and mixtures thereof. As is known to those of skill in the art, if it is desired to utilize ethyl aluminum sesquichloride as the organoaluminum cocatalyst, to is possible to produce the cocatalyst by mixing equimolar amounts of diethyl aluminum chloride and ethyl aluminum dichloride.

15 [0032] In a preferred embodiment of the invention, it is preferred to utilize a two component organoaluminum cocatalyst consisting of an alkyl aluminum chloride compound as described hereinabove (e.g., diethyl aluminum chloride, ethyl aluminum dichloride, ethyl aluminum sesquichloride and mixtures thereof) and an organo aluminum compound as described hereinabove (e.g., trimethylaluminum, triethylaluminum, diethyl aluminum hydride, triisobutyl aluminum, tri-
20 decyl aluminum, tridodecyl aluminum, diethyl aluminum methoxide, diethyl aluminum ethoxide, diethyl aluminum phenoxide, methyl diethoxy aluminum, methyl aluminoxane and mixtures thereof).

[0033] The third component of the present catalyst system is a catalyst activator having the formula:



wherein M is a metal selected from Group 2 and Group 12 of the Periodic Table, R⁷ is a C₁-C₁₂ alkyl group and n is a number equal to the valence of M.

30 [0034] Preferably, R⁷ is selected from the group comprising methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-hexyl, n-octyl, n-decyl and the like. More preferably, R⁷ is a C₁-C₆ alkyl group. Most preferably, R⁷ is an ethyl group.

[0035] Preferably, M is selected from the group comprising beryllium, magnesium, calcium, strontium, barium, zinc, cadmium and mercury. Most preferably, M is zinc.

35 [0036] Thus, non-limiting examples of compounds useful as a catalyst activator in the present catalyst system may be selected from the group comprising dimethyl zinc, diethyl zinc, dipropyl zinc, di-i-propyl zinc, di-s-butyl zinc, methylpropyl zinc, dipentyl zinc, methylpentyl zinc, dimethyl cadmium, diethyl cadmium, dipropyl cadmium, di-i-propyl cadmium, di-s-butyl cadmium, methylpropyl cadmium, dipentyl cadmium, methylpentyl cadmium, dimethyl mercury, diethyl mercury, dipropyl mercury, di-i-propyl mercury, di-s-butyl mercury, methylpropyl mercury, dipentyl mercury, methylpentyl mercury, dimethyl beryllium, diethyl beryllium, dipropyl beryllium, di-i-propyl beryllium, di-s-butyl beryllium, methylpropyl beryllium, dipentyl beryllium, methylpentyl beryllium, dimethyl magnesium, diethyl magnesium, dipropyl
40 magnesium, di-i-propyl magnesium, di-s-butyl magnesium, methylpropyl magnesium, dipentyl magnesium, methylpentyl magnesium, dimethyl calcium, diethyl calcium, dipropyl calcium, di-i-propyl calcium, di-s-butyl calcium, methylpropyl calcium, dipentyl calcium, methylpentyl calcium, dimethyl strontium, diethyl strontium, dipropyl strontium, di-i-propyl strontium, di-s-butyl strontium, methylpropyl strontium, dipentyl strontium, methylpentyl strontium, dimethyl barium, diethyl barium, dipropyl barium, di-i-propyl barium, di-s-butyl barium, methylpropyl barium, dipentyl barium, methylpentyl barium and mixtures thereof.

45 [0037] The most preferred activator for use in the present catalyst system is diethyl zinc.

[0038] The present catalyst system may be used to produce an olefin polymer. As used through this specification, the term Olefin polymer is intended to have a broad meaning and encompasses homopolymers, copolymers, terpolymers, etc. which are derived from the polymerization of at least one olefin monomer. As used throughout this specification, the term "olefin monomer" is intended to have a broad meaning and encompasses α-olefin monomers, diolefin monomers and monomers containing at least one internal olefin linkage.

[0039] In one preferred embodiment, the olefin monomer is ethylene.

55 [0040] In another preferred embodiment, the olefin monomer is an α-olefin monomer. α-Olefin monomers are well known in the art and the choice thereof for use in the present process is within the purview of a person skilled in the art. Preferably, the α-olefin monomer is selected from the group propylene, butene-1, isobutene, pentene-1, hexene-1, octene-1, branched isomers thereof, styrene, α-methylstyrene and mixtures thereof. The most preferred α-olefin monomer is propylene.

[0041] In yet another preferred embodiment, the olefin monomer comprises a diolefin monomer. Diolefin monomers

are well known in the art and the choice thereof for use in the present process is within the purview of a person skilled in the art. In one preferred embodiment, the diolefin monomer is an aliphatic compound. Non limiting examples of suitable aliphatic compounds may be selected from the group comprising 1,3-butadiene; isoprene; 2,3-dimethylbutadiene-1,3; 2-ethylbutadiene-1,3; piperylene; myrcene; allene; 1,2-butadiene; 1,4,9-decatrienes; 1,4-hexadiene; 1,6-octadiene; 1,5-hexadiene; 4-methylhexadiene-1,4; 5-methylhexadiene-1,4; 7-methyl-octadiene-1,6; 3,7-dimethyl-octadiene-1,6; 3,7-dimethyl-octadiene-1,7; phenylbutadiene; pentadiene and mixtures thereof. In another preferred embodiment, the diolefin monomer is an alicyclic compound. Non-limiting examples of suitable alicyclic compounds may be selected from the group comprising norbornadiene, alkyl derivatives thereof, 5-alkyldenenorbornene-2 compounds, 5-alkenyl-norbornene-2 compounds and mixtures thereof, such as 5-methylene-2-norbornene, 5-ethylidene-2-norbornene, 5-vinylidene-2-norbornene, 5-propenyl-2-norbornene and mixtures thereof. Further non-limiting examples of suitable alicyclic compounds may be selected from the group comprising 1,4-cyclohexadiene, 1,5-cyclooctadiene, 1,5-cyclododecadiene, methyltetrahydroindene, dicyclopentadiene, bicyclo [2.2.1] hepta-2,5-2,5-diene and mixtures thereof. The most preferred diolefin monomers may be selected from the group comprising 5-ethylidene-2-norbornene and 5-vinylidene-2-norbornene.

[0042] Of course it is possible, and preferred, to utilize mixtures of the various types of olefin monomers described hereinabove.

[0043] In one preferred embodiment, the olefin monomer is a mixture of ethylene and at least one α -olefin (as described hereinabove) which results in the production of a copolymer. The preferred such monomer mixture comprises ethylene and propylene. In this embodiment, it is preferred to utilize a mixture comprising in the range from 30 to 75, more preferably from 35 to 70 weight percent ethylene and in the range from 25 to 70, more preferably from 30 to 65 weight percent α -olefin.

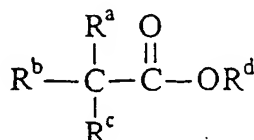
[0044] In another preferred embodiment, the olefin is a mixture of ethylene, at least one α -olefin (as described hereinabove) and at least one diolefin monomer (as described hereinabove) which results in the production of a terpolymer. The preferred such monomer mixture comprises ethylene, propylene and 5-ethylidene-2-norbornene. In this embodiment, it is preferred to incorporate into the preferred mixture of ethylene and α -olefin in the range from 0.5 to 15, more preferably from 1 to 12 weight percent of the diolefin monomer.

[0045] Polymerization of the olefin monomer(s) using the present catalyst system may be carried out in solution or suspension, preferably in suspension, in a polymerization medium containing a hydrocarbon (preferably a saturated hydrocarbon) in which the polymer is substantially insoluble. When the polymerization process is conducted in suspension, one of the reactants (e.g., the α -olefin, if used) may be used as the polymerization diluent or a hydrocarbon in which the product polymer is insoluble may be used as the diluent. Polymerization of the olefin monomer(s) may be carried out batchwise or in a continuous manner. The preferred process involves continuous slurry polymerization in which ethylene, α -olefin monomer, diolefin monomer (if used) and the catalyst system are continuously supplied to a reaction zone and the product polymer is formed as a slurry in the liquid phase. Suitable inert hydrocarbons for use as the polymerization medium are those selected from the group comprising C₃-C₈ aliphatic hydrocarbons, C₅-C₁₀ cyclic aliphatic hydrocarbons, C₆-C₉ aromatic hydrocarbons, C₃-C₈ monoolefinic hydrocarbons and mixtures thereof. Non-limiting examples of such hydrocarbons include: (i) straight and branched chain hydrocarbons such as propane, butane, isobutane, pentane, hexane, octane and the like; (ii) cyclic and alicyclic hydrocarbons such as cyclopentane, cyclohexane, cycloheptane, ethylcyclopentane, methylcyclohexane, methylcycloheptane and the like; (iii) alkyl-substituted aromatic hydrocarbons such as toluene, xylene and the like; and (iv) liquid olefins which may act as monomers or comonomers such as propylene, butene-1 and the like. The preferred hydrocarbon, if used, is propylene.

[0046] The choice of relative proportions of the vanadium (i.e., from the vanadium catalyst) and total aluminium (i.e., from the organoaluminum cocatalyst) is within the purview of a person skilled in the art. Thus, the ratio of the molar amount of the vanadium catalyst to the total molar amount of organoaluminum cocatalyst(s) is preferably in the range of from 1:5 to 1:1000, more preferably from 1:10 to 1:300, most preferably from 1:10 to 1:150.

[0047] The activator component of the present catalyst system should be added to the polymerization reaction in an amount sufficient to provide in the range from 0.0001 to 2.0 moles of activator per mole of olefin monomer (i.e., total molar amount of all olefin monomers if a mixture is used). The activator component may be added to the reactor dissolved in an inert liquid solvent. The inert liquid solvent should be nonreactive with the activator and the other components of the reaction mixture (i.e., the vanadium catalyst, the organoaluminum cocatalyst, etc.). Non-limiting examples of useful inert liquid solvents include isopentane, hexane, heptane, toluene, xylene and naphtha. Preferably, the solution added to the polymerization reaction contains the activator in an amount of in the range from 1 to 99, preferably from 2 to 25 weight percent.

[0048] Other additives conventionally used in Ziegler-Natta polymerization processes may be used in the present process. Thus, in some cases, it may be desirable and preferred, to add to the catalyst system a catalyst promoter. Non-limiting examples of suitable catalyst promoters include chlorinated hydrocarbons such as those having the general formula:



10 wherein:

R^a and R^b may be the same or different and are a halogen;

R^c is selected from the group comprising halogen, an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and an ester group; and

15 R^d is selected from the group comprising an alkyl group, an aryl group and an alkenyl group. Non-limiting examples of useful such chlorinated hydrocarbons include ethyl-trichloroacetate (ETA), dichlorophenyl ethyl acetate (DCPEE) and 2-halo malonic ester compounds such as diethyl 2-chloro-2-phenyl malonate.

[0049] The present process is generally carried out at temperatures in the range of from -40°C to 200°C , preferably from -20° to 100°C , more preferably from 0°C to 80°C , and at a pressure in the range of from 5 to 700 psig.

[0050] The precise mode of carrying out the present process is not particularly restricted. In one preferred embodiment, the present process may be carried out by first introducing the hydrocarbon diluent into a stirred tank reactor together with the olefin monomer(s) and adjusting the pressure of the reactor contents so that the temperature of the reactor contents are brought to the desired level. Ethylene gas may be introduced either into the vapour phase of the reactor or sparged into the liquid phase as is known in the art. Thereafter, a hydrocarbon solution of the vanadium compound and a hydrocarbon solution of the organoaluminum cocatalyst(s) in the desired ratios are introduced to the reactor. The polymerization occurs substantially in the liquid phase, a slurry of the product polymer being formed in the hydrocarbon diluent. The rate of polymerization may be controlled by the rate of catalyst addition. The reactor temperature and pressure may be controlled through the vaporization of the liquid phase as well as by cooling coils, jackets, etc. If a mixture of olefin monomers is used, the content of any one monomer in the polymer product may be controlled by manipulating the feed rates of the respective olefin monomers to the reactor and by manipulating the concentration of catalyst fed to the reactor. The polymer product may be recovered in a conventional manner by flashing off the lower boiling compounds either at reduced pressure or by treatment of the slurry with a mixture of steam and hot water, and by the use of a devolatilizing extruder or by further steam stripping and subsequent dewatering and drying. In a preferred continuous process, the mean residence time of the catalyst and polymer in the reactor is generally in the range from 20 minutes to 8 hours, preferably from 30 minutes to 6 hours, more preferably from 1 to 4 hours.

[0051] Embodiments of the invention will be illustrated with reference to the following Examples which are provided for illustrative purposes and should not be used to construe or limited the scope of the invention.

[0052] In the Examples, the weight percent ethylene in the polymer products was determined by Fourier Transform Infra Red (FTIR) spectroscopy. Thus, polymeric films were pressed at 150°C and the spectra recorded. The ethylene content was determined by integrating the absorbance peaks at 720 cm^{-1} and 1153 cm^{-1} , and performing the calculation using empirically derived relationships.

EXAMPLES 1-10

[0053] In these Examples, various ethylene-propylene copolymers were produced in a batch process under slurry conditions.

[0054] Polymerization was conducted in a one liter ZipperClave[®] reactor. As is known to those of skill in the art, this reactor is jacketed and stirred with an explosion-proof motor. The reactor was equipped with a series of independent syringe pumps to allow for introduction to the reactor of catalyst, cocatalyst, catalyst activator and catalyst promoter (if used) through separate feed streams. The reactor system was interfaced with a computer to facilitate direct data acquisition (e.g., polymerization temperature, ethylene flow, etc.).

[0055] The catalyst used in Examples 1-6 and 9-10 was $[(\text{CyH})_2\text{N}]_2\text{VCl}_2$ (CyH/cyclohexyl). This catalyst was produced in a conventional manner. The catalyst used in Example 7 and 8 was $\text{V}(\text{acac})_3$ (acac/acetyl acetone) which was produced in a conventional manner.

[0056] The cocatalysts used in these Examples were diethyl aluminum chloride (DEAC) or ethylaluminum sesquichloride (EASC). The catalyst activator, if used, was diethyl zinc (DEZ). The precise cocatalyst used in each Example and the presence/absence of DEZ is set out in Table 1. Further, a catalyst promoter in the form of a chlorinated hydrocarbon

was used.

[0057] The ZipperClave™ reactor was charged with an inert hydrocarbon diluent (240 mL), liquid propylene (250 mL) and pressurized with ethylene to a total pressure of 87-99 psig. After allowing the contents of the reactor to equilibrate to a temperature of 12°C, the vanadium catalyst containing catalyst promoter (molar ratio of promoter to vanadium was approximately 5:1) and organoaluminum cocatalyst were introduced to the reactor to provide the cocatalyst/catalyst molar ratio reported in Table 1, followed by addition of the catalyst activator DEZ (9.6 mL; 10 mM) for Examples 2, 4, 6, 8 and 10 only. Ethylene was supplied to maintain the initial total pressure in the reactor. The polymerization was carried out for up to 90 minutes after which any unreacted monomers were flashed off and the temperature of the reactor was raised to approximately 20°C. The polymer product was recovered with an alcohol and thereafter dried in a vacuum oven at 60°C.

[0058] As will be apparent to those of skill in the art, a catalyst activator (i.e., DEZ) was not used in Examples 1, 3, 5, 7 and 9. Accordingly, Examples 1, 3, 5, 7 and 9 are outside the scope of the present invention and are provided for comparative purposes only. As will be further apparent to those of skill in the art, since V(acac)₃ was used as the catalyst in Example 8, this Example is also outside the scope of the present invention and is provided for comparative purposes only.

[0059] In Table 1, there is reported the precise cocatalyst used, the cocatalyst/catalyst molar ratio, an indication of whether DEZ was used, the weight percentage of ethylene in the polymer product and the molecular weights (Mn and Mw) of the polymer product. The molecular weight of the polymer products was determined by gel permeation chromatography (GPC) at 140°C using trichlorobenzene as a solvent. The molecular weight is reported in Table 1 as polystyrene equivalents.

[0060] The results reported in Table 1 clearly demonstrate one of the advantages accruing from the use of diethyl zinc as a catalyst activator. Specifically, as will be apparent to those of skill in the art, at a given cocatalyst/catalyst molar ratio, the use of diethyl zinc provides desirable molecular weight control in the product when compared to the situation where diethyl zinc is not used in the process.

[0061] The results reported in Table 1 also clearly demonstrate another of the advantages accruing from the use of diethyl zinc as a catalyst activator in combination with a vanadium catalyst containing amide linkages to the metal. Specifically, as will be apparent to those of skill in the art, when DEZ is used as a catalyst activator, the catalyst efficiency of [(CyH)₂N]₂VCl₂ more than doubles when compared to the case where [(CyH)₂N]₂VCl₂ is used without DEZ and the molecular weight of the polymer product is desirably reduced when compared to the case where [(CyH)₂N]₂VCl₂ is used without DEZ - i.e., [(CyH)₂N]₂VCl₂ is more active with DEZ than without. Importantly, when DEZ is used as a catalyst activator, the catalyst efficiency of V(acac)₃ is reduced and the molecular weight of the polymer product is desirably reduced when compared to the case where V(acac)₃ is used without DEZ - i.e., V(acac)₃ is more active without DEZ than with DEZ. This is a surprising and unexpected result.

[0062] With further reference to Examples 1-10, increasing the cocatalyst/catalyst molar ratio from 70 to 280 results in a significant increase in catalyst efficiency when DEZ is used (i.e., Examples 2, 4 and 6) as a catalyst activator. In contrast, increasing the cocatalyst/catalyst molar ratio from 70 to 280 results in a slight change in catalyst efficiency when DEZ was not used as the catalyst activator (i.e., Examples 1, 3 and 5). This effect is illustrated in Table 2 in which selected data from Table 1 has been reorganized. Thus, the Examples illustrate that, in the absence of a catalyst activator as defined herein, increasing the cocatalyst/catalyst molar ratio does not necessarily result in an increased catalyst activity. This serves to further underscore the surprising and unexpected advantageous results accruing from the use of a catalyst activator such as DEZ.

TABLE I

Example	Catalyst	Co-Catalyst	Catalyst/Co-Catalyst Molar Ratio	DEZ Used (Yes/No)	Ethylene Content (wt.%)	Catalyst Efficiency (kg polymer/ mol V)	Molecular Weight ($\times 10^{-3}$)	
							Mn	Mw
1	$[(\text{CyH})_2\text{N}]_2\text{VCl}_2$	DEAC	70	N	70	1318	608	1294
2	$[(\text{CyH})_2\text{N}]_2\text{VCl}_2$	DEAC	70	Y	70	3171	227	548
3	$[(\text{CyH})_2\text{N}]_2\text{VCl}_2$	DEAC	140	N	70	1282	623	1620
4	$[(\text{CyH})_2\text{N}]_2\text{VCl}_2$	DEAC	140	Y	70	4020	290	714
5	$[(\text{CyH})_2\text{N}]_2\text{VCl}_2$	DEAC	280	N	71	1186	519	1319
6	$[(\text{CyH})_2\text{N}]_2\text{VCl}_2$	DEAC	280	Y	70	5173	390	860
7	$\text{V}(\text{acac})_3$	DEAC	35	N	66	4166	537	1423
8	$\text{V}(\text{acac})_3$	DEAC	35	Y	69	3108	151	523
9	$[(\text{CyH})_2\text{N}]_2\text{VCl}_2$	EASC	35	N	68	2282	902	2256
10	$[(\text{CyH})_2\text{N}]_2\text{VCl}_2$	EASC	35	Y	67	6800	705	2184

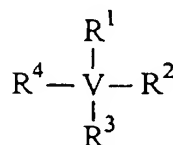
TABLE 2

Example	Al/V Molar Ratio	DEZ Used (Y/N)	Catalyst Efficiency (kg polymer/mol V)
2	70	Y	3171
4	140	Y	4020
6	280	Y	5173
1	70	N	1318
3	140	N	1282
5	280	N	1186

Claims

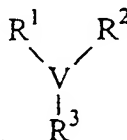
1. An olefin monomer polymerization catalyst system comprising:

(i) a vanadium catalyst having the formula:



wherein:

R^1 , R^2 , R^3 and R^4 are the same or different and each is selected from a halogen and $-(NR^5R^6)$, R^5 and R^6 are the same or different and each is selected from the group comprising an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and a silicon-containing hydrocarbyl group, and R^1 and R^2 may be combined to form a cyclic moiety, with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is $-(NR^5R^6)$, or the formula:



wherein:

R^1 , R^2 and R^3 are as defined above, with the proviso that at least one of R^1 , R^2 and R^3 is $-(NR^5R^6)$;

(ii) an organoaluminum cocatalyst; and

(iii) a catalyst activator having the formula:



wherein M is a metal selected from Group 2 and Group 12 of the Periodic Table, R^7 is a C_1 - C_{12} alkyl group and n is a number equal to the valence of M;

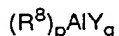
wherein at least one of the vanadium catalyst and organoaluminum cocatalyst contains a halogen moiety.

2. The catalyst system defined in claim 1, wherein R^1 and R^2 are the same or different and each is $-(NR^5R^6)$, and R^3 and R^4 are the same or different and each is a halogen.

3. The catalyst system defined in any one of claims 1-2, wherein the halogen comprises chloride.

4. The catalyst system defined in any one of claims 1-2, wherein each of R^5 and R^6 is selected from the group comprising an ethyl group, a propyl group, an *i*-propyl group, a butyl group and a cyclohexyl group.

5. The catalyst system defined in any one of claims 1-4, wherein the organoaluminum cocatalyst comprises at least one compound having the formula:



wherein R^8 is selected from the group comprising a C_2 - C_{20} alkyl group, a C_2 - C_{10} alkoxy group and a C_3 - C_{20} cycloalkyl group, Y is selected from the group comprising R^8 and a halogen and $p+q$ is 3.

6. The catalyst system defined in any one of claims 1-4, wherein the organoaluminum cocatalyst is selected from the group comprising trimethylaluminum, triethylaluminum, diethyl aluminum hydride, triisobutyl aluminum, tridecyl aluminum, tridodecyl aluminum, diethyl aluminum methoxide, diethyl aluminum ethoxide, diethyl aluminum phenoxide, diethyl aluminum chloride, ethyl aluminum dichloride, ethyl aluminum sesquichloride, diisobutylaluminum chloride, dioctylaluminum chloride, octylaluminum sesquichloride, methyl diethoxy aluminum, methyl aluminoxane and mixtures thereof.

7. The catalyst system defined in any one of claims 1-6, wherein the catalyst activator is selected from the group comprising dimethyl zinc, diethyl zinc, dipropyl zinc, di-*i*-propyl zinc, di-*s*-butyl zinc, methylpropyl zinc, dipentyl zinc, methylpentyl zinc, dimethyl cadmium, diethyl cadmium, dipropyl cadmium, di-*i*-propyl cadmium, di-*s*-butyl cadmium, methylpropyl cadmium, dipentyl cadmium, methylpentyl cadmium, dimethyl mercury, diethyl mercury, dipropyl mercury, di-*i*-propyl mercury, di-*s*-butyl mercury, methylpropyl mercury, dipentyl mercury, methylpentyl mercury, dimethyl beryllium, diethyl beryllium, dipropyl beryllium, di-*i*-propyl beryllium, di-*s*-butyl beryllium, methylpropyl beryllium, dipentyl beryllium, methylpentyl beryllium, dimethyl magnesium, diethyl magnesium, dipropyl magnesium, di-*i*-propyl magnesium, di-*s*-butyl magnesium, methylpropyl magnesium, dipentyl magnesium, methylpentyl magnesium, dimethyl calcium, diethyl calcium, dipropyl calcium, di-*i*-propyl calcium, di-*s*-butyl calcium, methylpropyl calcium, dipentyl calcium, methylpentyl calcium, dimethyl strontium, diethyl strontium, dipropyl strontium, di-*i*-propyl strontium, di-*s*-butyl strontium, methylpropyl strontium, dipentyl strontium, methylpentyl strontium, dimethyl barium, diethyl barium, dipropyl barium, di-*i*-propyl barium, di-*s*-butyl barium, methylpropyl barium, dipentyl barium, methylpentyl barium and mixtures thereof.

8. The catalyst system defined in any one of claims 1-6, wherein the catalyst activator comprises diethyl zinc.

9. The catalyst system defined in any one of claims 1-8, further comprising a catalyst promotor selected from the group comprising ethyl-trichloroacetate (ETA), dichlorophenyl ethyl acetate (DCPEE), diethyl 2-chloro-2-phenyl malonate and mixtures thereof.

10. A process for production of an olefin polymer comprising the step of polymerizing an olefin monomer in the presence of the catalyst system defined in any one of claims 1-9.

11. The process defined in claim 9, wherein the olefin monomer is selected from the group comprising ethylene, an α -olefin monomer, a diolefin monomer and mixtures thereof.

12. The process defined in claim 9, wherein the olefin monomer comprises a mixture of ethylene and at least one α -olefin monomer.

13. An olefin polymerization catalyst kit comprising, as individual components, (i) the vanadium catalyst, (ii) the organoaluminum cocatalyst, and (iii) the catalyst activator defined in any one of claims 1-8.

14. The olefin polymerization catalyst kit defined in claim 13, further comprising a catalyst promotor selected from the

group comprising ethyl-trichloroacetate (ETA), dichlorophenyl ethyl acetate (DCPEE), diethyl 2-chloro-2-phenyl malonate and mixtures thereof.

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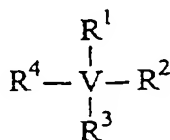
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(54) Olefin polymerization process and catalyst system therefor

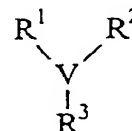
(57) An olefin monomer polymerization catalyst system is described. The catalyst system comprises:

(i) a vanadium catalyst having the formula:



wherein:

R^1 , R^2 , R^3 and R^4 are the same or different and each is selected from a halogen and $-(NR^5R^6)$, R^5 and R^6 are the same or different and each is selected from the group comprising an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group and a silicon-containing hydrocarbyl group, and R^1 and R^2 may be combined to form a cyclic moiety, with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is $-(NR^5R^6)$, or the formula:



wherein:

R^1 , R^2 and R^3 are as defined above, with the proviso that at least one of R^1 , R^2 and R^3 is $-(NR^5R^6)$;

(ii) an organoaluminum cocatalyst; and

(iii) a catalyst activator having the formula:



wherein M is a metal selected from Group 2 and Group 12 of the Periodic Table, R^7 is a C_1 - C_{12} alkyl group and n is a number equal to the valence of M. At least one of the vanadium catalyst and organoaluminum cocatalyst contains a halogen moiety. A process for polymerizing an olefin using the catalyst system is also described.



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EUROPEAN SEARCH REPORT

Application Number
EP 99 10 7520

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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Y	* page 8, line 19 - page 9, line 36; table 1 *	1-14	
X	EP 0 464 744 A (UNION CARBIDE CHEM PLASTIC) 8 January 1992 (1992-01-08) * page 6, line 15 - page 9, line 56; claim 14 *	1-3,5-8, 10-13	
Y	US 3 711 455 A (CUCINELLA S ET AL) 16 January 1973 (1973-01-16) * the whole document *	1-14	
Y	WO 95 00564 A (DSM NV) 5 January 1995 (1995-01-05) * page 9, line 17 - page 11, line 10 *	10,14	
Y	EP 0 712 871 A (UNION CARBIDE CHEM PLASTIC) 22 May 1996 (1996-05-22) * page 5, line 48 - page 5, line 50 *	10,14	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08F
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 17 November 1999	Examiner Van Golde, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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